Illumination-induced metastable polaron-supporting state in poly(*p*-phenylene vinylene) films

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We found an illumination-induced metastable polaron-supporting state in films of a soluble derivative of poly-*p*-phenylene vinylene (MEH-PPV). Pristine, nonilluminated MEH-PPV polymer films do not show long-lived photogenerated polarons. Prolonged UV illumination, however, is found to induce a reversible, metastable state characterized by its ability to support abundant long-lived photogenerated polarons. In the dark, the illumination-induced metastable state reverts back to the state of the original MEH-PPV within about 30 min at room temperature. Relying on the well-established ubiquitous reversible photoinduced cyclization of diarylethenes into dihyrophenanthrene derivatives, we propose a reversible mechanism in which UV illumination transforms *cis* native defects in the polymer chains into metastable deep traps that substantially increase the photogenerated polaron lifetime in the film.

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Photomodulation (PM) spectroscopy has served as a useful tool for investigating the nature of long-lived photogenerated charged polarons ($P^{\pm}$) and neutral triplet excitons (TEs) in π-conjugated polymers and oligomers.[1–4] In pristine polymers, the majority of the primary photoexcitations have been found to be singlet excitons. The excitons decay either nonradiatively or radiatively in the form of photoluminescence (PL) emission. Intersystem crossing to the triplet manifold is one of the most prominent nonradiative decay processes, leading to a long-lived triplet exciton that is characterized by a photoinduced absorption (PA) band in the near-IR spectral range. In contrast, when doped with electron acceptors such as C_{60},[5,6] contaminated by impurities, or defected by a reaction with oxygen in the dark,[7,8] then long-lived polarons are efficiently photogenerated via an ultrafast photoinduced charge transfer process. This is usually accompanied by an efficient reduction of the PL quantum yield and abundant photoinduced polarons at steady-state conditions that are characterized by two PA bands in the mid- and near-IR spectral ranges, respectively.

In this work we show that UV illumination (UVI) reversibly transforms a pristine MEH-PPV film, which does not support long-lived photogenerated polarons (denoted hereafter as "structure *A*"), into a metastable configuration that is capable of supporting polaron excitations (denoted hereafter as "structure *B*"). In the dark, the metastable structure *B* was found to revert back to the original structure *A* within about 30 min at room temperature. At lower temperatures, however, the recovery process is considerably longer, an indication of a thermally activated $B \rightarrow A$ back process. Relying on the well-established ubiquitous photoinduced cyclization of diarylethenes into dihydrophenanthrene derivatives, we propose a reversible mechanism in which UVI transforms native *cis* defects in the polymer chains into deep traps for photogenerated polarons.

PM spectra were obtained by measuring the differential transmission, $-\Delta T/T$, of the transmission T induced by a pump beam excitation at various temperatures, pump modulation frequencies and intensities, using a standard PM setup,[1] or a Fourier transform infrared PM spectrometer.[9] For fabricating the drop cast films we used pristine MEH-PPV powder with a narrow distribution of molecular weight, centered at 720 000 g/mol, which was supplied by American Dye Source (ADS).

Figure 1 shows the 80-K PM spectrum of a pristine MEH-PPV film (structure *A*) kept under vacuum in the dark over-

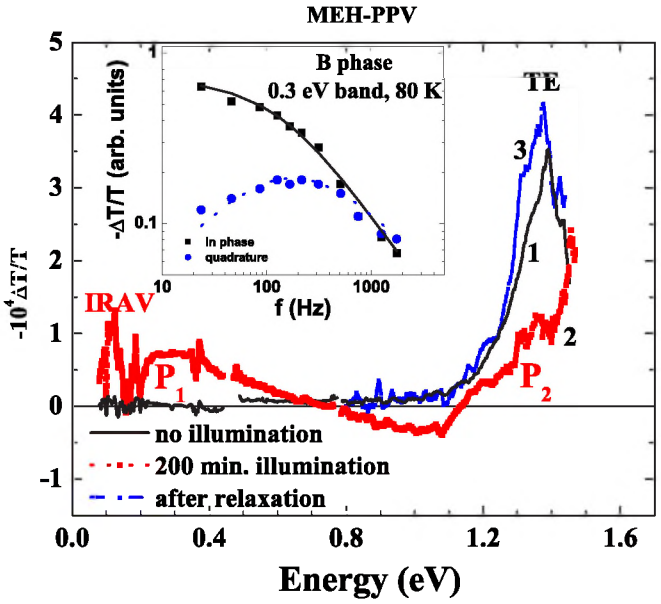

FIG. 1. (Color online) PM spectra of neat MEH-PPV film at 80 K upon UVI at 360 nm and 0.1 W/cm^2. Curve 1 (black solid line): before UVI (structure *A*). Curve 2 (red dotted line): after 200 min UVI (structure *B*). Curve 3 (blue dashed line): after overnight annealing at RT (structure *A* again). The inset shows the modulation frequency dependence of the polaron P_1 in structure *B*. The solid (dotted) line is a fit of the in-phase (quadrature) component using a dispersive recombination model (Refs. 14 and 15) with an average lifetime of 0.9 ms and dispersive parameter $\alpha \cong 0.73$.

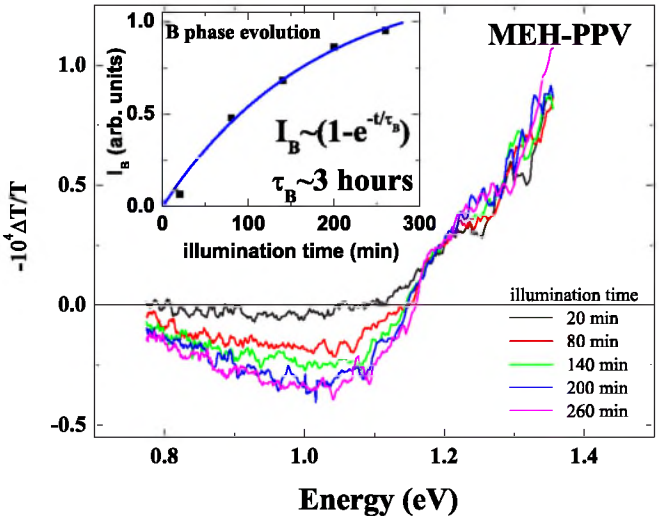

FIG. 2. (Color online) The PB band related to polarons in structure B at various UVI times t as indicated. The inset shows the strength I_B of the PB band vs t. The line through the data points is a fit to a saturation behavior (see text).

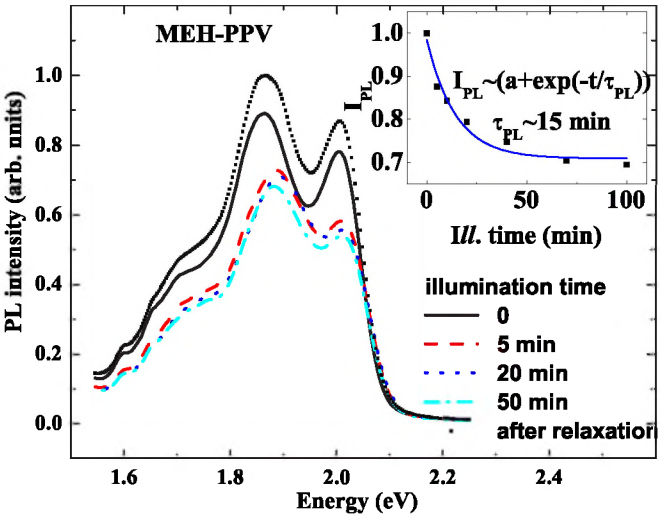

FIG. 3. (Color online) PL spectra of MEH-PPV film at 80 K under UVI exposure at 360 nm and 0.1 W/cm^2 for time duration t as indicated. The insert shows the PL intensity I_{PL} vs t; the line through the data points is a fit (see text).

night (curve 1). The PM spectrum is dominated by a single PA band at $\sim$1.35 eV ascribed as due to TEs;[10] other PA bands due to photogenerated polarons are not detected in this unilluminated film. Figure 1 also contains (curve 2) the PM spectrum measured at the same experimental conditions, but after the pristine film was subjected to UVI ($\sim$0.1 W/cm^2 at 362 nm, total dose of $\sim 3\times10^{21}$ photons), which transform some of its chromophores into different moieties (structure B). This new PM spectrum differs substantially from that of structure A. It shows two distinct *polaron-related spectroscopic features*: (i) photoinduced IR-active vibrations (IRAV) below 0.2 eV and (ii) a low-energy PA band P_1 centered at $\sim$0.3–0.4 eV. Furthermore, the PA band related to the TE is considerably weaker, as a shoulder at $\sim$1.3 eV. Also, a new photobleaching (PB) band (i.e., $\Delta T/T>0$) appears between 0.8 and 1.2 eV. The new polaron features; namely, the IRAV and P_1 bands and the PB band scale with each other at various excitation intensities, as well as with the duration of UVI. The transition energies of the observed IRAV lines and the P_1 band are very close to those measured for polarons in films of MEH-PPV/C_{60} composites,[10] strongly suggesting that they indeed originiate from photoexcited polarons. The energy range of the PB band is in agreement with the observed transition photon energy of bipolarons in MEH-PPV.[11] As argued below, UVI sets up the conditions for photoexcitation of polarons. Polarons that are created by continuous UVI have a finite probability to form bipolarons, which are more stable[11] and therefore are trapped deeper than polarons. Thus, the PB band may originate from the photobleaching of these deeply trapped bipolarons, explaining its scaling with the polaron transitions (IRAV and P_1).

We studied the transformation of structure A into structure B with UVI time t by measuring the PB and P_1 bands associated with structure B at various UVI times [see Fig. 2 for PB(t)]. Figure 2, inset, shows the polaron induced structure B component, I_B as measured by PB(t). It is clearly seen that the A-to-B structure transformation is slow, following a saturation-type curve $I_B \propto [1-\exp(-t/\tau_B)]$, with $\tau_B \sim 3$ h (equivalent to UVI of $\sim 3\times10^{21}$ photons at 362 nm).

The blue dashed line (curve 3) in Fig. 1 represents the PM spectrum of the same film measured with the same experimental conditions, but after the film was annealed in the dark at room temperature overnight, under vacuum (10^{-5} Torr). Comparing the PM spectrum of the annealed film to that of the original film, it is clear that structure B completely disappears, reverting the MEH-PPV film to its original pristine structure A, of which the PM spectrum is again dominated by the TE band. We thus conclude that upon UVI, the pristine MEH-PPV film (structure A) transforms into a metastable structure B, which then reverts in the dark to the original structure A.

We can estimate the density N of the UVI-induced polarons using the relation $\Delta T/T = N\sigma d$, where σ is the absorption cross section and d is the sample thickness. Taking $\Delta T/T \sim 10^{-4}$ observed for the P_1 band at 0.3 eV, $\sigma = 10^{-15}$ cm^2,[12] and $d = 100$ nm, we find that the UVI-induced polaron density at saturation is $\sim 10^{16}$ cm^{-3}.

The time it takes for the MEH-PPV film in structure B for reverting to structure A was studied at ambient and liquid nitrogen temperatures. We found that $\sim$30 min at room temperature suffices to completely revert back to structure A, whereas at 80 K we could not detect any recovery to structure A even after the sample in structure B was left in the dark for over 2 h.

The UVI also affects the strength of the PL emission band (Fig. 3). It is clearly seen that the PL band substantially weakens upon UVI, but its spectrum does not change much. The PL decrease is summarized in Fig. 3 (inset), where the PL intensity I_{PL} is plotted vs the UVI time t. $I_{PL}(t)$ may be fit by the function $I_{PL} \propto [a+\exp(-t/\tau_{PL})]$, with $\tau_{PL} \sim 15$ min. That the PL spectrum stays robust under UVI shows that its weakening upon illumination is not induced by any effect related to conjugation length interruption, such as carbonyl

defects. Otherwise, the PL spectrum would have blue shifted with UVI and be irreversible. Similar to the PM spectrum recovery mentioned above, the PL intensity regains its original strength associated with structure *A* when the film is annealed in the dark at room temperature.

A comparison of the rates τ_{PL}^{-1} and τ_P^{-1} (Fig. 2, inset) indicates that the PL emission decreases much faster than the appearance of the polaron PA bands in structure *B*. This indicates that the defects created by UVI and/or the trapped polarons at these defects are very efficient PL quenchers.

The steady-state PA signal is proportional to the product of the photogeneration quantum efficiency (QE) and the lifetime (τ) of the relevant photoexcited species:

$$\mathrm{PIA} \propto I_L \times \mathrm{QE} \times \tau, \tag{1}$$

where I_L is the pump intensity. Therefore the long-lived polaron PA bands seen in structure *B* may originate from either a large increase in QE or a dramatic lifetime increase of short-lived polarons that are originally photogenerated in structure *A*.[13] In order to separate these two possible underlying causes, we measured the polaron dynamics in structure *B* and compared it with the polaron dynamics of polarons in structure *A*.[13] Figure 1 (inset) shows the modulation frequency dependence of the lower polaron band P_1 in structure *B* measured at 0.3 eV. An average lifetime τ_0 of ~1 ms is extracted from the frequency $f_{\max}$ (~200 Hz) at the maximum of the quadrature component where $\tau_0 \sim 1/(2\pi f_{\max})$.[14,15] On the other hand, previous time-resolved PM measurements of pristine MEH-PPV in structure *A* revealed the existence of short-lived polarons with lifetime ~1 ns.[13] We thus conclude that the polaron lifetime in structure *B* films is about 10^6 times longer than that of free polarons in structure *A* films. This strongly indicates that the enhanced polaron PA in the steady-state PM spectrum of structure *B* is in fact caused by a *lifetime* increase rather than an induced increase in photogenerated polaron quantum efficiency. The dramatic polaron lifetime increase in structure *B* may be due to charge trapping into efficient deep traps that are photogenerated in the polymer chains upon UVI. We offer the following model for explaining the origin of these metastable deep traps.

Relying on the well-established ubiquitous reversible photoinduced cyclization of diarylethenes into dihydrophenanthrene systems, we propose a reversible defect formation mechanism in which UVI creates metastable deep defects from *cis* native defects in the polymer chains. Such *cis* defects may be either naturally present in the MEH-PPV film or created by UVI [Fig. 4(A_1,A_2)]. UVI-induced deep defects are actually new species in the film with shifted highest occupied and lowest unoccupied molecular orbital (HOMO) and (LUMO) levels. Thus, holes and electrons have a different electronic affinity, enabling the new species to act as traps for holes (*upward shift of HOMO-LUMO levels*) or electrons (*downward shift*), or both (*HOMO downward, LUMO upward*), thereby substantially increasing the photogenerated polaron lifetime (Fig. 4). In analogy with the well-documented photocyclization of Z-stilbene derivatives into dihydrophenanthrene derivatives,[16] we propose that Z-diphenyl ethene [*cis*-diphenyl ethane, Fig. 4(A_2)] defects

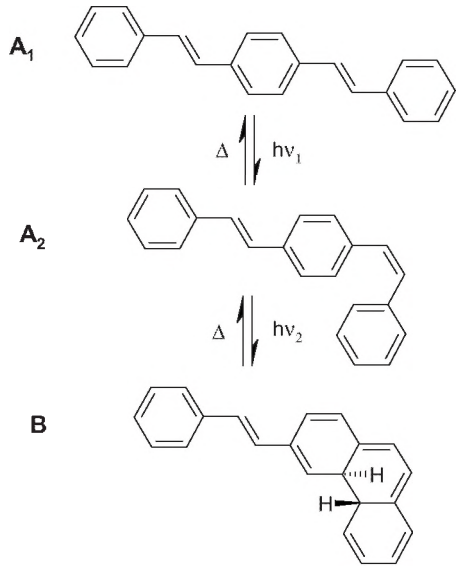

FIG. 4. The proposed reversible mechanism for the UVI-induced "polaron-supporting state" (structure *B*). Shown schematically are the relevant segments of MEH-PPV. (A_1) trans configuration. (A_2) cis defect. (B) UVI-induced charge trap that dominates structure *B* films.

of the polymer chain, which are known to exist in phenylene-vinylene based oligomers,[17,18] undergo a photochemically allowed cyclization into dihydro phenanthrene containing segments [Fig. 4(B)]. These polymer segments are still conjugated. In the dark, the dihydrophenanthrene skeleton (structure *B*) undergoes a thermally induced ring opening, thus reverting to the *cis*-diphenyl ethene structure (structure *A*). This reaction in the dark is characterized by typical lifetimes that may vary from seconds to months at room temperature. Pristine MEH-PPV in structure *A* constitutes segments of *cis*-diphenyl ethene species. MEH-PPV in Structure *B* includes segments of *B* species due to photocyclization. This kind of *reversible* photocyclization was reported to occur in oligomers as well as in polymeric species.[16,19] The dihydrophenanthrene photoproduct [Fig. 4(B)] acts as a deep trap for charge carriers, leading to long-lived opposite-charge polarons on the MEH-PPV polymer chains. The observed density of UVI-induced polarons (see above) puts a reasonable upper limit of $\sim 10^{16}$ cm^{-3} for the *cis* defects concentration in structure A polymers.

The present mechanism for the UVI-induced reversible formation of deep traps accounts for all experimental observations, as summarized below.

(i) PM spectra of nonirradiated pristine MEH-PPV film (structure *A*) do not show long-lived photogenerated polarons, since the *A* species [native *cis* defects, Fig. 4(A_2)] do not trap polarons.

(ii) UVI of the pristine film leads to steady-state PM spectra that show new peaks characteristic of polarons, related to the new form *B* [Fig. 4(B)], which acts as a charge trap.

(iii) In the dark, the UVI-induced *B* structure reverts to the pristine *A* structure in a thermally activated manner.

In summary, we found a UVI-induced metastable polaron supporting state in neat MEH-PPV films. The pristine films in their original structure *A* show strong PL emission and

long-lived photogenerated triplet excitons, but no long-lived polarons. Prolong exposure to UVI reversibly transforms parts of the pristine films into a different structure *B*, in which long-lived polarons are photogenerated and the PL emission is considerably quenched. Structure *B* films transform back to the original structure *A* films with a temperature-dependent recovery time of ~30 min at room temperature and many hours at liquid nitrogen temperature. We propose a plausible mechanism by which UVI reversibly transforms native *cis* defects in the polymer chains into deep charge traps.

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